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A quantitative study of ZnO materials as possible down-shifters for solar cell applications

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Abstract

We report about a systematic study of nanocrystalline ZnO which exhibits intensive blue-green defect luminescence after annealing in reducing atmosphere. The ZnO has been dispersed in a polymer and tested with a commercial Si solar cell. A quantitative model including photoluminescent quantum efficiency, absorption and backscattering has been developed and compared with measurements of the ZnO-coated cell. We find that strong backscattering from the ZnO layer leads a reduced efficiency of the system except for a small enhancement in the UV region. Necessary conditions for achieving overall improvements in cell efficiency are derived.

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Keywords: Down shifting; ZnO; defect luminescence; luminescent quantum efficiency; silicon cell; efficiency

1. Introduction

Single crystalline photovoltaic cells based on silicon nowadays have reached efficiencies of up to 25 % which is quite close to the efficiency limit predicted by Shockley and Queisser for the limit of only radiative recombination as a source of charge carrier loss [1]. One of the limitations of the efficiency of single junction photovoltaic cells

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originates from the compromise between non-absorption of solar photons with energies below the band gap of the semiconductor, and the requirement of achieving a large cell voltage (which is in general increasing with increasing band gap). Practical limitations also arise from the non-radiative recombination processes at the front and back surface of the cell, which can be minimized by surface passivation and back surface grading techniques. Considering the principal limitations pointed out by Shockley and Queisser, it appears attractive to modify the spectrum of sunlight [2] by down-conversion before it enters the solar cell, by generating multiple photons out of one absorbed photon. The non-absorption of low-energy photons could be solved in principle by up-conversion of 2 or more transmitted photons to higher energies which lie within the absorption range of the cell material. However, both approaches still suffer from limited conversion efficiencies of the required converter materials, or the requirement of extremely high light intensity. Taking into account the practical limitations of real solar cells mentioned above, it appears that even plain down-shifting of photons (i.e. generating one photon with lower energy from an absorbed high-energy photon) may be beneficial if the relative gain in cell performance at the lower photon energy is large enough.

In this paper, we have studied the possible application of ZnO as a down-shifter material for Si solar cells. ZnO has a band gap energy of 3.37 eV at room temperature, which falls into the range where there is still considerable intensity in the solar spectrum, but where standard Si cells do not perform well. To act as a down-shifter, luminescence of the ZnO in the visible range is desired. It has been shown over the years [3-6] that such luminescence can be achieved in ZnO nanostructures due to the presence of defects. It has already been demonstrated that ZnO nanoparticles can be used for down-shifting [7], which may also be useful for increasing the sensitivity range of photosensitive devices [8]. In this paper, we present a detailed study of ZnO nanoparticles embedded in a polymer (polydimethysiloxane, PDMS). Spin-coated films with different amounts of ZnO have been characterized using photoluminescence, and subsequently applied as converters in front of a standard crystalline Si cell under AM1.5 illumination. In addition, we have measured spectrally resolved photocurrents of the cells under monochromatic illumination over a wide range of wavelengths starting at 300 nm. The experimental data are used to determine the input parameters for a quantitative modelling of the efficiency of the combined system (converter plus cell). The model can describe the changes of the overall system efficiency reasonably well. It is used to identify the necessary conditions to achieve an overall system efficiency increase by using ZnO as a down-shifter. The main requirement is the reduction of backscattering losses induced by introduction of the ZnO layer, together with a further increase of the luminescent quantum efficiency of the nanoparticles.

2. Experimental methods

ZnO is a semiconductor with a direct band gap of 3.37 eV. It has been shown previously that intense luminescence in the visible range can be achieved by introducing defects. This can be done in different ways, among them is annealing in a reducing atmosphere, which generates oxygen vacancies. In [9], a correlation between the density of (singly ionized) oxygen vacancies and the emission strength in the green wavelength region has been observed. In this study, we use commercially available ZnO nanopowders (Alfa Aesar, 99.99 % purity) which were annealed at 700°C in a quartz tube furnace in a H_2/Ar (1:1) atmosphere at a total flow rate of 2 slm for 80 min. These conditions have been previously identified to yield maximum luminescence intensity [10]. We find a slight agglomeration of the particles after the treatment, with an average size of the agglomerates of around 210 nm as verified by scanning electron microscopy.

After annealing, the ZnO particles were embedded in PDMS (polydimethylsiloxane) films. The particles were first mixed with the surfactant dioctyl sodium sulfosuccinate at a constant ratio of 4:1 to avoid additional agglomeration. A varying amount of the ZnO/surfactant mixture was then stirred together with isooctane (15 g) for 15 minutes at 1200 rpm. Then, 4.4 g of PDMS were added and the whole mixture was again stirred for 40 minutes at 1200 rpm. Finally, the dispersion was ultrasonicated to break up and re-disperse large particle agglomerates. Dynamic light scattering measurements confirm a final particle size of around 200-250 nm. A set of dispersions with a different volume fraction of ZnO ranging from nominally ~0.3% to ~3% were produced (here, the term volume fraction always means the nominal volume fraction of ZnO in the initial mixture). These dispersions were spin-coated on microscope glass slides at 1000 rpm for 20 seconds and baked at 100°C for 4 hours to obtain solid PDMS films containing different amounts of ZnO. To determine the amount of ZnO in the films, X-ray fluorescence (XRF) measurements (using a ComPact eco by Roentgenanalytik Systems) were performed on the coated glass slides. For calibration of the absolute

amount of ZnO, reference XRF measurements of a sputtered Zn film of known thickness were used. The XRF measurements show that the amount of Zn in the films is linearly proportional to the initial ZnO volume fraction.

The optical properties of the ZnO have been determined by photoluminescence (PL) measurements performed in a Horiba Flurolog 3 spectrofluorometer using a Xenon lamp (OSRAM XBO 450W OFR) for excitation and a photomultiplier tube (R928) for detection. For quantum efficiency measurements, we used a self-made integrating sphere coated with barium-sulphate. The band-width of the excitation and emission monochromators were set to 0.5 nm and 3 nm, respectively. The step width of the secondary monochromator (between sample and detector) was set to 3 nm. This setup has also been used to determine transmission and absorption of the PDMS layers with varying amounts of ZnO. For quantitatively measuring the effect of different coatings on the performance of a Si cell, a standard solar cell with an area of 3 cm² was measured inside a solar simulator (LOT-Quantum Design) under AM 1.5 illumination using a 300 W Xenon lamp. The I-V characteristics of our monocrystalline Si solar cell (Conrad YH-26X46) were measured by a Keithley 4200 semiconductor characterizing system. All measurements were performed with the same solar cell just by exchanging the PDMS-coated glass slides. For external quantum efficiency (EQE) measurements, we used a custom-built setup. For short wavelengths ($\lambda < 580$ nm), a 150 W Xenon lamp (Mueller electronics) was used, and a Halogen lamp for long wavelengths ($\lambda > 580$ nm). The light is modulated by an external chopper and then sent through a tunable monochromator (Horiba). The beam is then split into two parts, which are guided by optical fibres to a reference detector and the Si solar cell, which are both connected to a lock-in amplifier driven by the chopper signal. The reference detector consists of a Si/InGaAs tandem cell which has a calibrated spectral response SR_{Ref} over a wavelength range of 320 nm - 1800 nm.

3. Results and discussion

For the determination of the luminescent quantum efficiency (LQE), which is defined as the number of emitted photons in the visible range $N_{em,vis}$ divided by the number of absorbed UV photons $N_{abs,UV}$ ($LQE = N_{em,vis}/N_{abs,UV}$), the intensity reflected from thick layers of annealed ZnO powders placed inside the integrating sphere was measured as a function of wavelength. For comparison, a neutral scatterer (Al_2O_3 powder) was measured under identical conditions. The results are shown in fig. 1a. The overall shape of the spectra reflects the spectral intensity of the light source. It can be observed that the ZnO powder absorbs the majority of photons below a wavelength of 376 nm corresponding to the band edge energy. In addition, a reduction of the reflected intensity in the visible range is found, which can be attributed to a small absorption of the annealed ZnO in the visible range. Fig. 1b shows the emission intensities from the ZnO powder under excitation with various wavelengths, and the well known blue-green emission with a maximum around 500 nm. Using both sets of data, it was possible to derive the LQE by dividing the total number of photons emitted over the whole range of wavelengths detected by the number of photons absorbed.

A further calibration step was done by using a known standard (YAG:Ce with approximately 98 % quantum efficiency, provided by OSRAM) to account for uncertainties in the secondary monochromator transmission function. After that, a curve of LQE vs. excitation wavelength was obtained as shown in fig. 2. It was found that the LQE increases with decreasing wavelength, and reaches a maximum value of 35 % at 280 nm. This value is very similar to the estimated LQE of about 30 % for ZnO nanopowders under excitation with 244 nm given in [7]. The observed increase of the LQE at shorter wavelengths might be attributed to the fact that the absorption length is expected to decrease with decreasing wavelengths, which would lead to absorption and emission in a thinner surface region of the ZnO powder. This would reduce the amount of self-absorption of luminescent intensity by the ZnO powder (see discussion fig. 1a) and therefore lead to an increase of the LQE value.

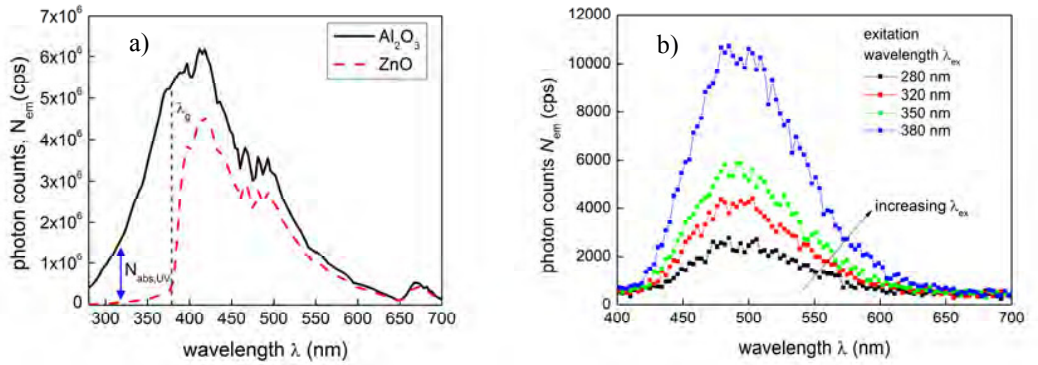

Fig. 1a (left) Reflected intensity of the annealed ZnO powder in comparison with the Al_2O_3 reference sample over a range from 280 to 700 nm. 1b (right) Emission intensity from the ZnO powder under excitation with various wavelengths.

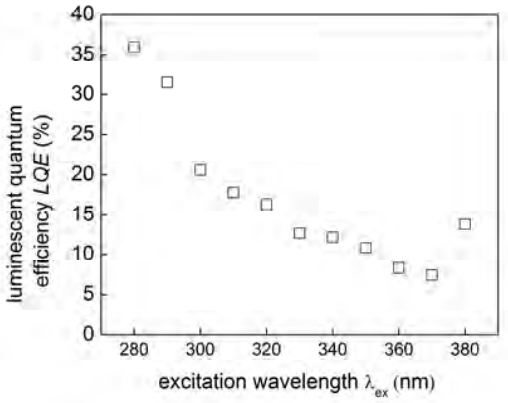

Fig. 2 Luminescent quantum efficiency of the ZnO nanopowders for excitation under different wavelengths.

In the next step, the transmission through the PDMS-coated glass slides with different amounts of ZnO in the PDMS was measured as a function of the wavelength. The transmitted intensities are normalized to the transmission of a glass slide coated with PDMS without ZnO nanoparticles. The results are shown in fig. 3. From the step in the curves at the band edge (marked by λ_g) the absorption A by the ZnO can be determined. We found a linear increase of the absorption with the volume fraction of ZnO. In addition, the amount of backscattered and absorbed light B in the visible region can be determined from the difference in transmission in the visible range (marked with labels a-d in fig. 3). Again, we found that this loss of transmitted intensity (hereafter it will by termed backscattering, since this fraction is expected to be the dominant part in the "optically thin" samples investigated here) increases linearly with the volume fraction of ZnO.

The next step towards a quantitative modelling is the characterization of the solar cell. This was done by an EQE measurement using a calibrated reference cell as described above. The result is shown in fig. 4. Here, the EQE is defined as EQE = N_{el}/N_{ph} where N_{el} is the number of electron-hole pairs generated, and N_{ph} is the number of photons absorbed. In addition, the spectral response S is obtained as defined by the current in mA per Watt of incident power. We observed a sharp drop of the EQE below 400 nm, which is typical for crystalline Si solar cells. It implies that the UV part of the solar spectrum does not contribute efficiently to the total output power of the cell.

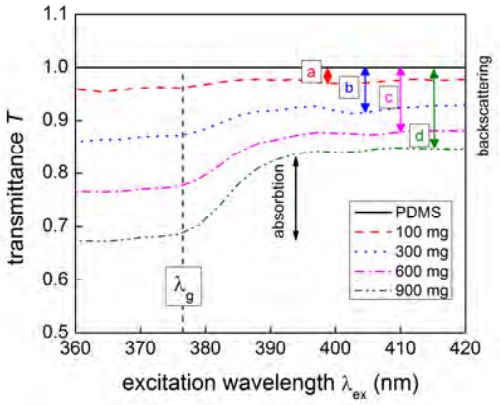

Fig. 3 Intensity transmitted through the PDMS-coated glass slides with various amounts of ZnO, normalized to the intensity transmitted through a glass slide coated with plain PDMS without ZnO nanoparticles. The numbers in the inset indicate the total amount of ZnO in the initial mixture.

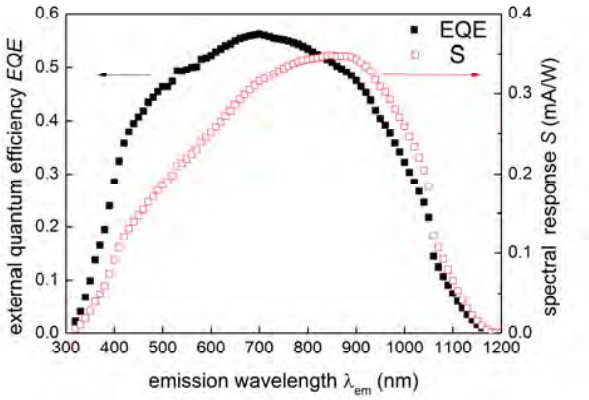

Fig. 4 Spectral response S and external quantum efficiency (EQE) of the Si cell used in the present study.

We have also characterized the EQE and the spectral response of the cell with and without glass slides and PDMS coating. Fig. 5 a shows the EQE of the bare cell without glass cover in comparison with the cell covered with the glass/PDMS/ZnO system. Over a wide range of wavelengths, a reduction of the EQE is evident. However, the situation is different in the UV region below 330 nm. Since the plain glass slides can already absorb UV light significantly in this wavelength range, the measurements were performed with the ZnO/PDMS-coated sides of the slides pointing towards the light source to minimize the effect of absorption in the glass. As shown in fig. 5b, in this wavelength region an increase of the short circuit current I_{SC} at a given wavelength by up to a factor of 3.8 at 300 nm can be observed. This reflects the fact that the ZnO converts UV photons, which do not lead to a significant photocurrent in the plain Si cell into visible light which lies within the range of high EQE.

To investigate the effect of the ZnO/PDMS coating on the overall cell efficiency, we have recorded I-V curves under AM 1.5 illumination as described above. The results are shown in fig. 6 for the different amounts of ZnO in the initial mixture. Not unexpectedly, introducing the glass slide already leads to a significant reduction of the photocurrent. This can be attributed to the reflection of light at the glass slide surface. This effect could be avoided by directly coating the PDMS on the Si cell. However, since the purpose of the present study is a quantitative modelling of the system, we found it more appropriate to use coated glass slides since this allows a quantitative determination of the absorption and transmission of the PDMS/ZnO layers. Coating the glass slides with pure PDMS leads to a slight

increase of the photocurrent, which indicates a reduced light reflection as a consequence of the slightly lower index of refraction of the PDMS (n = 1.43) in comparison to the glass (n = 1.52). Introduction of the ZnO leads to a reduction of the photocurrent which increases with the amount on ZnO. This can be understood by the fact that the back reflection of visible light by the ZnO as shown in fig. 3 dominates above the photocurrent increase in the region below 330 nm.

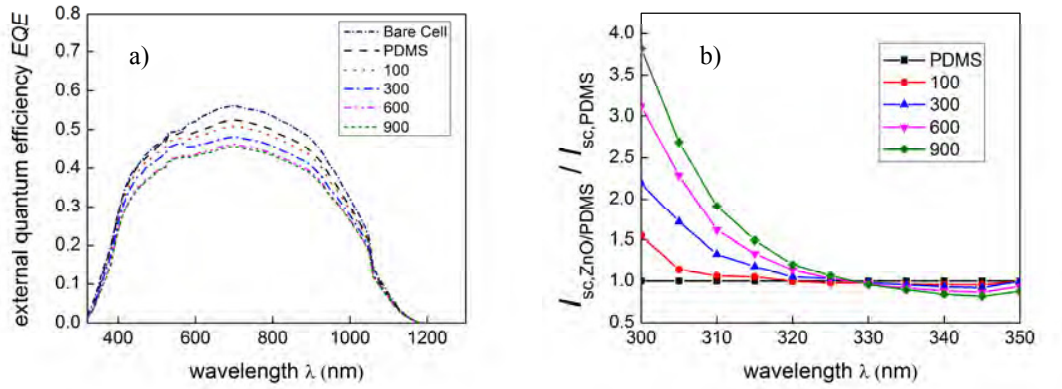

Fig. 5a (left) EQE measurement of the bare Si cell without glass cover in comparison with the cell covered with PDMS coated glass slides containing no ZnO (termed "PDMS" here) or various amounts of ZnO as indicated by the numbers (numbers have the same meaning as in fig. 3). 5b (right) Ratio of short circuit currents with ($I_{SC,ZnO/PDMS}$) or without ($I_{SC,PDMS}$) ZnO in the PDMS layer.

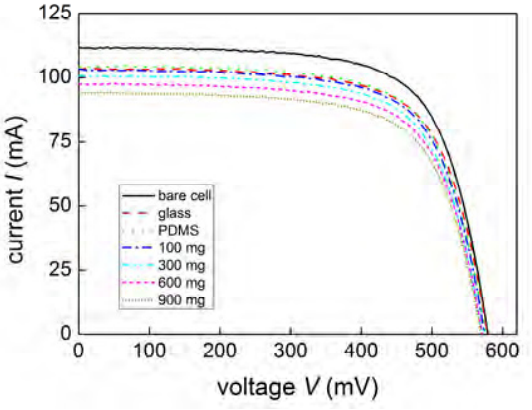

Fig. 6 I-V curves of the Si cell without glass slide ("bare cell"), or covered with plain ("glass") or PDMS ("PDMS") coated glass slide, as well as covered with glass/PDMS/ZnO systems with varying amount of ZnO in the initial mixture.

The next step is now to quantitatively model the effect of the ZnO included in the PDMS layer (termed LDS for luminescent down shifter hereafter). The model used here includes consideration of the absorption of UV light from the solar spectrum by the ZnO, conversion with an efficiency expressed by the LQE, and absorption and backscattering of light as shown in fig. 3. The short-circuit current is estimated by integrating over the incident spectrum. In fig. 7 a schematic drawing of the combined LDS/solar cell system is given. The system is illuminated by sunlight with an incoming number of photons (per area, time and wavelength interval) N(λ) which is given by the solar spectrum (approximated by black body radiation at T = 5800 K).

The LDS layer is characterized by the UV absorption A, the backscattering B and the luminescent quantum efficiency LQE. A linear dependence on the volume fraction v of ZnO in the PDMS layer is considered for the backscattering B (B = βv, with β the backscattering coefficient) and the absorption A (A=φv, with φ the absorption

factor). The actual values of β and φ have been obtained from a fit to the experimental absorption and backscattering vs. v. While the backscattering is assumed to be independent of the incident wavelength, the absorption is assumed to be 0 for energies lower than the band gap. The LQE has been directly taken from the measurement shown in fig. 2. Finally, the spectrum modified by the LDS layer and reaching the solar cell N_{mod} is given by the sum of directly transmitted photons N_{trans} and the absorbed and re-emitted photons N_{em}.

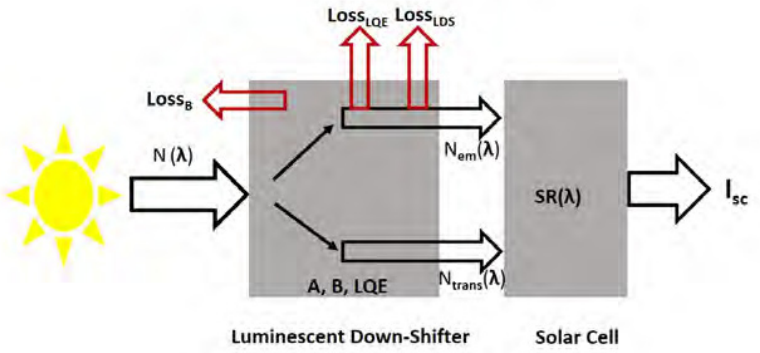

Fig. 7 Schematic illustration of the photon loss, conversion and transmission processes used for description of combined LDS/solar cell system.

$$N_{\mathrm{mod}}(\lambda) = N_{trans}(\lambda) + N_{em}(\lambda) = N(\lambda)\left[(1-B)\cdot(1-A) + (1-B)\cdot A\cdot(LQE(\lambda))\right] \quad (1)$$

The modified spectrum is now taken as a new incident spectrum for the solar cell with spectral response S(λ). This results in a short-circuit current I_{sc} which is calculated by:

$$I_{SC} = A_c \int_{280nm}^{1500nm} N_{\mathrm{mod}}(\lambda)\, E_p(\lambda)\, S(\lambda)\, d\lambda \quad (2)$$

where $E_p(\lambda)$ is the energy of a photon at wavelength λ and A_c is the area of the solar cell. Fig. 8 shows the relative change of photocurrent $(I_{SC,mod} - I_{SC})/I_{SC}$, where I_{SC} and $I_{SC,mod}$ refer to the short-circuit currents calculated according to eq. 2 for the unmodified or the modified spectrum, respectively. The model does correctly predict a continuous decrease of I_{SC} with increasing amount of ZnO. For comparison, the measured relative changes of I_{SC} are also shown. It can be observed that the general trend of the experimental data is reproduced quite well. The differences between experimental and predicted I_{SC} values may be attributed to the fact that the angular dependence of the scattered intensity as well as the details of the propagation of light in the PDMS/ZnO/glass system are not treated in sufficient detail in the present model. We point out here that the present model overestimates the losses, leading to lower values of the predicted I_{SC} than the actually measured ones. We may therefore use the model to estimate the conditions under which an overall efficiency gain under AM 1.5 illumination may be expected. Due to the overestimation of the losses, the estimates obtained in this way should be considered as sufficient, but an efficiency increase may be achieved even under slightly relaxed conditions.

As an example, fig. 9 shows an overview diagram of the predicted relative change of photocurrent as a function of the backscattering coefficient β for different LQE values. A value of φ = 6.02 has been used to calculate the absorption, which is identical to the value determined from the experimentally measured absorption (see fig. 3). The ZnO volume fraction is v = 0.027, which is close to the maximum volume fraction in our experiments. The green line (LQE_{exp} in fig. 9) has been calculated using the experimentally determined LQE values of our ZnO powder (see fig. 2). To illustrate the effect of a variation of LQE, we made calculations assuming constant LQE over the wavelength interval from 280 to 380 nm (this approximation appears reasonable for the case of optically thin ZnO films, since the transmission below 377 nm (see fig. 3) does not vary much with the wavelength and self absorption of the re-emitted visible light should not play a significant role for optically thin samples). A positive relative change of photocurrent

means a gain in cell performance, whereas negative values mean that the LDS layer leads to a performance loss. From fig. 9, we find that for the Si cell used here performance gain would be possible even for an LQE of only 40 % (LQE = 0.4 line in fig. 9), provided that the backscattering coefficient can be reduced to $\beta < 0.08$. The backscattering coefficient of the present ZnO/PDMS LDS layer is around 5.33, which is in the loss region even for a hypothetical LQE of 100 %. It is clear that under the present experimental conditions it is not possible to obtain an efficiency increase. The main reason for the strong backscattering can be found in the differences of the index of refraction between PDMS (n = 1.43) and ZnO (n varies between 2 and 2.5 in the visible). Better matching of the index of refraction, e.g. by choosing a better suited film material, could provide better perspectives for a performance increase under AM 1.5 illumination. Alternatively, incorporating the ZnO into the Si cell structure (e.g. embedding into the silicon nitride anti-reflection layer, or in between the Si nanowires in future nanowire solar cells) could also provide a solution to the backscattering problem in the future.

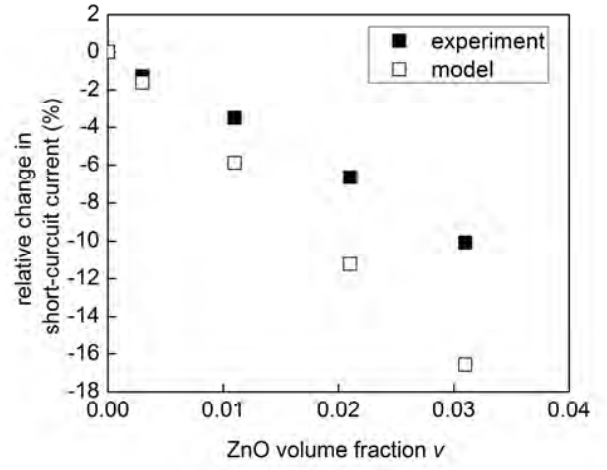

Fig. 8 Results for the relative change in short-circuit current from the model calculations using equation 2 (open squares) in comparison with the experimental results (filled squares).

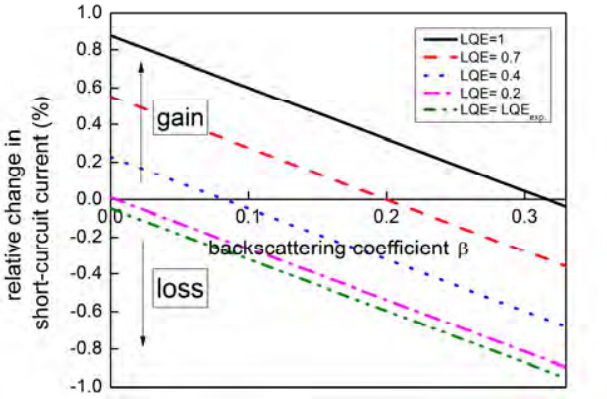

Fig. 9 Relative change of short-circuit current vs. backscattering coefficient calculated according to equation 2 for different values of luminescent quantum efficiency LQE. A volume fraction of $v = 0.027$ was used for the calculation.

4. Conclusion

We have studied the application of ZnO as a possible down-shifter material for Si solar cells. We have determined the luminescent quantum efficiency (LQE) of the material after an annealing treatment in reducing atmosphere, and find values of up to 38 % depending on the excitation wavelength. By placing glass slides coated with this material in front of a standard monocrystalline Si solar cell, an enhancement of the spectral response in the UV regime from 300 to 330 nm was observed. Under AM 1.5 illumination, a reduction of the photocurrent which increases with ZnO volume fraction was found. A simple model for the effect of the ZnO on the solar spectrum has been developed which is based on the measured transmission and backscattering of the ZnO, as well as the measured wavelength dependent LQE. For the cell used here, it was found that the strong backscattering observed always leads to an overall loss of cell efficiency under AM 1.5 illumination, which is in accord with the experimental results. We find that a reduction of the backscattering by more than a factor of 10 is required for an efficiency increase. It appears attractive to integrate the luminescent ZnO nanoparticles directly into the solar cell, which can be expected to avoid the backscattering losses to a large extent.

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